

AD-A258 118

OFFICE OF NAVAL RESEARCH

Grant N00014-91-J-1274

R&T Code 413m005—04

Technical Report # UMR-FDB-27

Effects of Water on the Interface  
in a Model Composite System An NMR Study

by

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Prepared for Publication in  
Materials Science and Engineering

November 1, 1992

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# REPORT DOCUMENTATION PAGE

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1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE 11-01-92		3. REPORT TYPE AND DATES COVERED Interim 11/91 - 11/92	
4. TITLE AND SUBTITLE  Effects of Water on the Interface				5. FUNDING NUMBERS  PE-N0014-91  PR-1274	
6. AUTHOR(S)  Joan E. Gambogi and Frank D. Blum					
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) University of Missouri-Rolla Department of Chemistry Rolla, MO 65401 ATTN: Frank D. Blum				8. PERFORMING ORGANIZATION REPORT NUMBER  UMR-FDB-#27	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) Office of Naval Research - Code 5000 Chemistry Division 800 Quincy Street Arlington, VA 22217 ATTN: Kenneth J. Wynne				10. SPONSORING / MONITORING AGENCY REPORT NUMBER	
11. SUPPLEMENTARY NOTES  For Publication in Materials Science and Engineering					
12a. DISTRIBUTION / AVAILABILITY STATEMENT  Approved for unlimited public release				12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words)  The molecular motion of the interfacial material in a model polymer composite has been probed and quantitatively described based on deuterium NMR studies. The system consisted of a silica surface (Cab-O-Sil), an aminobutylsilane coupling agent (aminobutylsilane-d <sub>2</sub> , DABS) which was labelled with deuterium in the β position, and a polymer matrix (bismaleimide). The addition of water to the system increased the molecular mobility of the surface-bound coupling agent. The motions of the coupling agent adsorbed on amorphous silica were simulated using a two-site jump model with tetrahedral jumps. For the coupling agent at the air interface, jump rates increased from 1.0 x 10 <sup>6</sup> s <sup>-1</sup> for the dry sample, to 4.0 x 10 <sup>6</sup> s <sup>-1</sup> for the sample in contact with water. For the sample with BMI reacted over it, the jump rate increased from 1.7 x 10 <sup>5</sup> s <sup>-1</sup> for the dry system to 5.0 x 10 <sup>5</sup> s <sup>-1</sup> for the wet system. The motional rate increase for both systems was a factor on the order of 3-4 with the addition of water. Deuterium exchange experiments were conducted between adsorbed aminobutylsilane and D <sub>2</sub> O. This resulted in the deuteration of the amino-group. The motions of the amino group were only slightly faster than those of the labelled methylene segment. Silicon-29 NMR was used to probe the effects of water. The results were consistent with the breaking of Si-O-Si bonds and increased mobility at the Si end of the coupling agent. All systems appeared to returned to their original state when the sample was dried.					
14. SUBJECT TERMS  Coupling agents, composites				15. NUMBER OF PAGES 24	
				16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT Unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	20. LIMITATION OF ABSTRACT		

## Abstract

The molecular motion of the interfacial material in a model polymer composite has been probed and quantitatively described based on deuterium NMR studies. The system consisted of a silica surface (Cab-O-Sil), an aminobutylsilane coupling agent (aminobutylsilane- $d_2$ , DABS) which was labelled with deuterium in the  $\beta$  position, and a polymer matrix (bismaleimide). The addition of water to the system increased the molecular mobility of the surface-bound coupling agent. The motions of the coupling agent adsorbed on amorphous silica were simulated using a two-site jump model with tetrahedral jumps. For the coupling agent at the air interface, jump rates increased from  $1.0 \times 10^6 \text{ s}^{-1}$  for the dry sample, to  $4.0 \times 10^6 \text{ s}^{-1}$  for the sample in contact with water. For the sample with BMI reacted over it, the jump rate increased from  $1.7 \times 10^5 \text{ s}^{-1}$  for the dry system to  $5.0 \times 10^5 \text{ s}^{-1}$  for the wet system. The motional rate increase for both systems was a factor on the order of 3-4 with the addition of water. Deuterium exchange experiments were conducted between adsorbed aminobutylsilane and  $D_2O$ . This resulted in the deuteration of the amino-group. The motions of the amino group were only slightly faster than those of the labelled methylene segment. Silicon-29 NMR was used to probe the effects of water. The results were consistent with the breaking of Si-O-Si bonds and increased mobility at the Si end of the coupling agent. All systems appeared to returned to their original state when the sample was dried.

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## 1. Introduction

The interface between the polymer matrix and the fiber plays a crucial role in the performance of polymer-reinforced composites. The role of the interface is to transmit the load from the matrix to the fibers, which have the greater strength and thus carry the load [1]. A weak interface may result in composite failure. Strong interfacial bonding is essential for transverse strength and environmental resistance. It is difficult to define and characterize the interfacial region in composite materials because it is usually so thin. It is often observed that moisture has a damaging effect on the strength of the interface and this becomes even more pronounced at high temperatures [2]. Other detrimental environmental factors include exposure to corrosive atmospheres, low and high temperatures, impact and ozone. Environmental factors may influence the fiber, matrix and the interface. This often results in changes in composite performance.

It is impractical, if not impossible, to keep moisture away from the interface in most materials, and therefore it is important to understand its effects. Water is adsorbed on anhydrous oxides and converted to hydroxyl groups. Molecular water is often held at the surface by hydrogen bonding to the surface hydroxyls. Most physically and chemically adsorbed water is not removed from the surface, unless heated to around 800 °C in vacuum for a few hours [2]. Even if composites are prepared under very dry conditions, in service, water may penetrate to the interfaces by diffusion through the polymers. An interface that is treated with the proper coupling agent may protect the polymer and the filler from hydrolytic deterioration. Silane coupling agents are used extensively to improve the interfacial bonding between inorganic fibers and polymer matrices and are particularly effective in the presence of water.

In order to understand the mechanical properties of composites in a fundamental way, it is necessary to know something about the motions which occur at a molecular level. Spectroscopic techniques are well suited for this molecular information and their application to composite interfaces has been reviewed. [3] An understanding of the molecular dynamics, that is, the way molecules move and respond to stress, should be invaluable in the design of interfaces for specific

applications. Generally, motions at the molecular level are difficult to qualify, and even more difficult to quantify.

In this paper, we describe experiments which were designed to probe the mobility of an interfacial layer of silane coupling agents and its response to water. The silane coupling agents were chemisorbed on a silica surface and probed at their interface in the presence of both air and a polymer. Thus, one of the systems studied was a model composite. The probe of the mobility of the interface relies critically on two factors. The first is the ability to interpret NMR spectra in terms of their motional information. The second is the ability to use an NMR active isotope to provide the necessary contrast--so that the interface can be probed even in the presence of materials of very similar composition. This allows all the labelled regions of the sample to be probed. Neither optical clarity, nor high vacuum are required.

Nuclear magnetic resonance techniques have made a large contribution in the efforts to probe different ranges of molecular motions. One approach used with solids and liquid crystals, is wide-line deuterium ( $^2\text{H}$ ) NMR [4,5]. This method provides a site specific, relatively non-perturbing probe for local molecular motions. Simulations of the experimentally determined line shapes test yields plausible models for the mechanism and frequency of molecular-level motions. The use of NMR to probe interfaces in polymeric systems [6] as well as the use of enriched species at the interfaces [7] have been reviewed. Since deuterium resonates at a very different NMR frequency than protons, there is no interference from the naturally abundant isotope of hydrogen, so that the position of the deuterons in the sample determine where the dynamics will be probed.

A variety of NMR techniques have been used to probe the interfaces modified with alkyl silanes. Isotopes of low natural abundance such as  $^{13}\text{C}$  [8-13] and  $^{29}\text{Si}$  [14-18] or both [19-24] have provided evidence for bonding and mobility for the surface-bound species. Carbon-13 studies have shown that a motional gradient exists for fairly long alkyl chains. Silicon-29 studies demonstrate that covalent bonding occurs with surface silanols and the spectra are diagnostic of the chemically distinct species formed. Unfortunately, the overlap of the resonances due to various

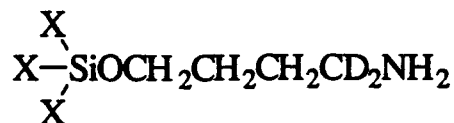
carbon species, make it difficult to analyze complex systems. In addition, for composites, the presence of a carbonaceous matrix swamps out the signals from the surface-bound species unless specific  $^{13}\text{C}$  labelling is used [25]. Silicon-29 NMR can be surface selective, but only gives information on the behavior of one end of the molecule.

One technique which has both good sensitivity and surface selectivity is  $^2\text{H}$  NMR. Deuterium NMR has already been used to study the molecular motions of silanes adsorbed on silica [26-34]. Through the use of line shape analysis, these studies have verified the motional gradient in the silanes, and probed changes in the local environment such as those created by different solvents. In addition, the contrast provided by the deuterium label was used to probe the surface layer in the presence of a polymer overlayer [33]. We have extended these studies of a model composite system to probe the effects of water on the interfacial mobility. Deuterium NMR lineshapes of the coupling agents were obtained and then compared to simulated line shapes. Solid-state  $^{29}\text{Si}$  NMR was also used in order to examine the nature of the silicon bonding and how this changes in the presence of water.

## 2. Experimental

### 2.1 Materials and Sample Preparation

Aminobutyltriethoxysilane (ABES) was used as received from Petrarch Systems, Inc. (Bristol, PA). After hydrolysis, the ethoxy groups react and are referred to simply as aminobutylsilane (ABS). Aminobutyltriethoxysilane- $d_2$  (DABES) was prepared from 2-cyanoethyltriethoxysilane (Aldrich, Milwaukee, WI) via the method previously described [29,33,35]. After hydrolysis, the material is referred to as aminobutylsilane- $d_2$  (DABS) and its structure is:



where the X's are representative of -OH, -OSi, or -OCH<sub>2</sub>CH<sub>3</sub> groups.

Fused silica (Cab-O-Sil grade S-17, nominal surface area 400 m<sup>2</sup>/g) was donated by Cabot Corporation and dried a minimum of two days at 110 °C prior to use. The deposition of the coupling agent was conducted according to the procedure previously described [29,31]. A 2.0% solution of the DABES was hydrolyzed in acetone/distilled water (10/1) for 3.5 hours. A 7 ml aliquot of this solution was then added to 0.15 g of the silica in a 15 ml centrifuge tube. The tube was shaken on a vortex mixer for 1 min, tumbled at a rate of 20 cycles/min for 15 min and centrifuged at 2000 rpm for 45 min. The treated silica was washed twice with distilled water to remove loosely held siloxanes and then dried in a vacuum oven at 90 °C for 12 h. It was previously determined that this preparation corresponded to approximately monolayer coverage [30,31]. The approximate amount of coupling agent present was calculated and reacted with an excess of bismaleimide resin, 1,1'-(methylenedi-4,1-phenylene)bismaleimide (BMI), (Aldrich) which was used as received.

The water treatment experiments were conducted using deuterium depleted H<sub>2</sub>O from Isotec, Inc. (purity ca. 5 ppm D). Liquid water was added directly to some of the samples in 5 mm wide-line NMR tubes. Boiling water tests were done by placing the sample in a 20 ml glass vial, adding

water, and refluxing for several hours. The contents were cooled to room temperature and then added to the tube wet. Deuterium exchange experiments were conducted by adding D<sub>2</sub>O to the sample in a 20 ml glass vial. The samples were allowed to equilibrate for around 8 h, and then dried thoroughly in a vacuum oven.

## 2.2 NMR Studies

A Varian VXR-200 NMR spectrometer was used for all the solid-state experiments. The deuterium wide-line experiments were done at 30.7 MHz using a quadrupole echo pulse sequence. The typical 90° pulse length was 2 μs with a repetition time about 0.5 s. A modification of the quadrupole echo pulse sequence was used:

$$[180_x \text{ (alternate pulses)} - \text{delay} - 90_x - \tau_1 - 90_y - \tau_2 - \text{echo}]_n$$

and contains a 180° prepulse and alternate subtractions to reduce coherent noise and acoustic ringing. The quad echo delays were typically 40 μs. In spite of this, small artifacts believed to be due to acoustic ringing were observed at about ± 120 kHz. This was problematic because of the low signal intensity due to the dilution effect of the silica [6]. Consequently, the spectra of the adsorbed coupling agents were taken with 30 000 to 40 000 scans for adequate signal to noise.

The solid-state <sup>29</sup>Si spectra were taken at room temperature on the VXR-200, at 39.7 MHz. The samples were packed into a zirconia or Vespel rotor and spun at the magic angle at 2 to 2.5 kHz. Cross polarization was used with a contact time of 2.5 ms and a recycle time of 3 s. A total of 20 000 scans were accumulated and the spectra externally referenced relative to liquid tetramethylsilane.

Two FORTRAN programs were used for the lineshape simulations. The first is based on models for discrete jumps between sites and was developed by Wittebort, Olejniczak and Griffin [36]. The program calculates the chemical exchange spectra for powders assuming an echo sequence is used for detecting the signal. Corrections are made for finite pulse width and distortions arising from the delay time between pulses. The second program was supplied by D.J.



Schneider and is based on the theory developed by Freed for slow motional electron spin resonance (ESR) lineshapes [37,38] for Brownian and jump diffusion, or a combination of both. This program has been modified by us to calculate deuterium lineshapes [39].

### 3.0 RESULTS

Deuterated aminobutyltriethoxysilane (DABES) was synthesized from cyanopropyltriethoxysilane and this resulted in the amino group and the carbon next to the amino group being deuterated [29]. Upon hydrolysis, the amino deuterons exchange with water leaving the coupling agent primarily deuterated on the penultimate carbon. After adsorption on and subsequent reaction with silica, the wide-line deuterium quadrupole-echo spectrum of the DABS on the surface is shown in Fig. 1A. The width of the resonance at half-height is about 68 kHz and lineshape is similar to that previously reported. For a sample with the same preparation 70 kHz was found previously [33] while 74-78 kHz was found for samples hydrolyzed from H<sub>2</sub>O [30]. These differences are probably due to small differences in oligomerization during the hydrolysis and adsorption process.

#### <Figure 1>

The sample of DABS on the silica surface was treated in boiling H<sub>2</sub>O and left wet. The resulting <sup>2</sup>H spectrum is shown in Fig. 1B. A narrower resonance, with a half-width reduced to ca. 38 kHz for the wet sample was observed. In addition, the rounded top of the resonance was observed to become pointed in the presence of water. This is believed to be due to small amounts of deuterium in the water which resulted in a very narrow signal. After the sample was redried, a spectrum almost identical to the original sample one was obtained (Figure 1C).

The simulated spectra shown in Fig. 1 were generated using a two-site jump about a rotational diffusion axis tilted at 54.75° and includes a contribution from slow anisotropic Brownian rotational diffusion ( $R_{||} = 7.0 \times 10^4 \text{ s}^{-1}$ ,  $R_{\perp} = 1.0 \times 10^4 \text{ s}^{-1}$ ) (30,33). The simulated spectrum for the dry sample at room temperature was calculated using a jump frequency of  $1.0 \times 10^6 \text{ s}^{-1}$ , and the lineshape of the wet sample was simulated using a jump rate of  $4.0 \times 10^6 \text{ s}^{-1}$ . In fitting the spectrum from the wet sample, the best fit was obtained by keeping the Brownian diffusion tensor terms constant and varying the jump rate.

When bismaleimide (BMI) resin was polymerized over the chemisorbed DABS on silica the spectrum in Fig. 2A was observed. The width of the resonance at half height of this spectrum was

ca. 113 kHz and it increased to about 120 kHz near the base. Upon treatment with boiling H<sub>2</sub>O, the resonance was observed to narrow substantially as seen in Fig. 2B. Again, a very narrow resonance was observed from the water treated sample which probably arose from water deuterons. Upon drying, the sample returned to nearly its original state as seen in Fig. 2C.

<Figure 2>

Consistent with earlier studies [33], the line shapes are fundamentally different from those of Figure 1. The motion believed to be responsible for this type of line shape is a two-site jump on a tetrahedral lattice. The spectra in Fig. 2 are simulated with hopping between unequally populated sites (0.70:0.30) and differing rates. Rates of  $1.7 \times 10^5 \text{ s}^{-1}$  fit the original and dried spectrum, while an increased rate of  $5.0 \times 10^5 \text{ s}^{-1}$  is required for the wet sample. In the presence of water, the upper half of the experimental line shape is reduced, while the lower perpendicular edges are still present. This feature is maintained in the simulated line shape with a change in rate alone.

In order to probe the mobility of the ND<sub>2</sub> group on the coupling agent, normal (protonated) ABS was adsorbed onto silica and then washed with D<sub>2</sub>O. The sample was then dried and the resulting <sup>2</sup>H NMR spectrum is shown in Figure 3A. Under these conditions, some of the deuterons and the amino hydrogens should have exchanged to yield the ND<sub>2</sub> species [29]. The motions of the deuterons on the amino group of the adsorbed coupling agent are comparable to the labelled methylene deuterons of DABS. The line width at half height is about 62 kHz and the spectral width at the base is 167 kHz. The line shapes obtained for samples hydrolyzed in D<sub>2</sub>O, then washed in D<sub>2</sub>O, are similar to those obtained from samples hydrolyzed in H<sub>2</sub>O and then washed in D<sub>2</sub>O. For comparison, the spectrum of DABS on the surface is shown in Figure 3B.

<Figure 3>

In order to probe the effects of water on the point of attachment of the coupling agent to the surface, <sup>29</sup>Si NMR was used. Shown in Fig. 4 is the <sup>29</sup>Si NMR spectra of DABS adsorbed on silica for both dry (Fig. 4A) and wet (Fig. 4B) samples. For the dry sample, in particular, the resonances were somewhat broad due to the inhomogeneous nature of the material and the slow

spinning rates. This inhomogeneity is in part due to the nature of the Cab-O-Sil silica [22]. The assignments can be based on a variety of studies [14-24]. The resonance due to the silicon atoms on the surface showed a predominance of the species  $\text{Si}(\text{OSi})_4$  (Q4) at -110 ppm and a contribution from  $\text{Si}(\text{OSi})_3\text{OH}$  (Q3) at -103 ppm. The relative intensity of the  $\text{Si}(\text{OSi})_3\text{OH}$  resonance increased when the sample was wet. The silicon from the coupling agent is predominantly  $\text{R}'\text{Si}(\text{OSi})_3$  and resonates at -65 ppm. From this spectra alone one cannot assign the siloxane bonds due to the silica surface versus bonds to other ABS molecules. The method of sample preparation, however, should remove any loosely bound molecules and provide close to a monolayer coverage. There is no discernable amount of physisorbed ABS present, which would resonate at 45 ppm. The spectrum of the wet sample shows more distinct environments of the coupling agent and is narrower due to increased molecular motion. Still predominant is the species  $\text{R}'\text{Si}(\text{OSi})_3$  (-66 ppm) with amounts of  $\text{R}'\text{Si}(\text{OSi})_2\text{OH}$  (-60 ppm) and  $\text{R}'\text{Si}(\text{OSi})(\text{OH})_2$  (-52 ppm). The presence of five or six coordinate silicon atoms can be excluded as they would resonate from -140 to -200 ppm [40]. Upon drying of the sample, the spectrum (not shown) returns to its original state.

#### Figure 4>

The  $^{29}\text{Si}$  spectra for the coupling agent adsorbed on silica that have been overpolymerized with BMI are quite similar to those without the BMI. A comparison of the spectra from the dry (Fig. 4C) and wet (Fig. 4D) composite samples also show increased intensity for silanol species with the addition of water. It is clear from the spectra, that the water penetrates and affects the silicon end of the coupling agent even in the presence of the polymer.

#### 4. Discussion

Molecular motions which occur on a  $10^{-3}$  to  $10^{-8}$  s time scale, can be discriminated through analysis of deuterium line shapes [41-44]. This is comparable with the time scale of many dynamic processes that occur in solids such as lattice jumps or rotational diffusion. The magnitude of the quadrupole splitting,  $\Delta_q$ , for a deuteron with an axially symmetric electric field gradient is given by [3,4]:

$$\Delta_q = 3/4 (e^2qQ/h) (3 \cos^2 \theta - 1) \quad (1)$$

where  $(e^2qQ/h)$  is the quadrupole coupling constant and  $\theta$  is the angle between the electric field gradient at the deuterium nucleus and the external magnetic field. In general, the superposition of the splittings from a distribution of angles  $\theta$  determine the line shape [4-5]. In a liquid, where there is rapid molecular motion, the term  $(3 \cos^2 \theta - 1)$  normally averages to zero. Motions in a solid may cause a partial averaging of this term, and the resultant line shape can be used to distinguish between different types of motion. Quadrupole coupling constants are usually about 165 kHz for aliphatic deuterons and 184 kHz for aromatic deuterons attached to carbons [44].

In either the fast or slow motion regime, the prediction of the line shape is easy, but in the intermediate regime, it is far from trivial. The operative timescale here is the reciprocal of the deuterium quadrupole coupling constant. Fortunately, theories have been worked out for some of these intermediate motions for simple mechanisms [36-38]. Determination of the rate and mechanism relies on the matching of a simulated and experimental lineshape. These "fits" are not necessarily unique, but may provide valuable insight to the types of motion present, especially if other types of motion can be excluded.

From previous studies [33], it has been shown that the effect of the polymerization of BMI over surface-bound coupling agents leads to both a change of the mechanism of coupling agent motion, as well as a general slowing of that motion. It is interesting to note that the effect of water at the interface appears to increase the rate of motion, but it does not appear to change the mechanism. Thus, the spectra for the coupling agent at the air interface are consistent with

anisotropic rotational diffusion plus conformational jumps. The polymerization and reaction with BMI freezes out the anisotropic rotational motion and the spectra become consistent with jumps only, with sites of unequal population.

The presence of water at the air-coupling agent interface narrows the deuterium line shape consistent with an increase in the jump rate by a factor of about four. When the sample is redried, it returns to its original state. Therefore, it appears that no permanent effects are seen in the deuterium line shapes because of treatment with water.

At the polymer-coupling agent interface, the effects of water are similar to those observed at the air-coupling agent interface. As expected, water penetrated the sample and migrated to the interface. Its effect on the  $^2\text{H}$  spectra in the composite provided confirmation of this in the composite system. The mobility of the coupling agent increases by about a factor of three as compared to the dry sample. This is quite close to the factor of four for the air-coupling agent interface. It is interesting that these increases are quite similar considering that one has a cross-linked polymer matrix present. These effects are superimposed on a slowing of roughly one order of magnitude due to the presence of the polymer. Again, when the sample is dried, the interface returns to its original mobility.

The effects of solvents on the mobility of other silanes have been studied. Short chain deuterated-alkoxysilanes on silica gel were investigated by Kelusky and Fyfe [26]. They found hexane and benzene had only a limited effect on the deuterium lineshape. In the presence of solvent, the original lineshape was superimposed on a narrow resonance. When methanol was added, the isotropic resonance dominated the spectrum. They attributed this narrow spectral component to a portion of the alkoxysilane being solubilized. Since the effect was greatest with methanol they concluded that the treated silica surface is fairly polar.

For other longer-chain surface-bound silanes, Gangoda and Gilpin found that the addition of solvent significantly increased the mobility of  $^{13}\text{C}$  labelled methylenes compared to the dry state [45]. Relaxation times for the bound silanes also correlated well with solvent viscosity for labelled

dodecyldimethylchlorosilane [46]. They also found two distinct types of solvent effects and attributed them to penetration of the solvent into the alkyl chains. The authors also suggested that the silanes were more orientationally ordered in the presence of solvents.

Unlike the system of Kelusky and Fyfe [26], the presence of solvent (water) did not lead to a particularly mobile species which could correlate with solubilized coupling agent. This difference may be due to the differences in silanol functionality in their compound (monofunctional) and ours (trifunctional). If a single -O-Si- bond is broken with the addition of water, another may keep the molecule in close proximity to the surface site so that rebonding may occur. In contrast to Gilpin and Gangoda's work, the wet surface-bound coupling agents appear to have the same type of motion, with only the rates changing. This is probably due to the shorter chain used in our coupling agents.

It has previously been shown that the amino hydrogens of the silane coupling agent exchange with  $D_2O$  [29]. Kang et al. studied the *bulk polymer* of deuterated-aminopropylsilane (DAPS) and APS- $ND_2$  with  $^2H$  NMR and showed that the motion of the deuterons on the amino group was much faster than that of the deuterons on the methylene group. It appears that on the surface, the mobility of the  $ND_2$  moiety is not much different from the methylene group when they are attached to silica. Our results are more consistent with the coupling agents extending vertically from the surface, while in the bulk polymer the alkyl chains have much more conformational and motional freedom.

The  $^{29}Si$  NMR spectra indicate a variety of silicon environments. Since cross polarization was utilized, only those silicon nuclei which were near a hydrogen resulted in a signal. For non-porous silica beads, most silicon atoms are in the interior and not near the protons which are on the surface. Consequently, the technique is inherently surface selective for this system.

A comparison of the wet and dry  $^{29}Si$  spectra indicates the formation of a higher percentage of silanol species. These silanol species can only be formed with the breakage of -Si-O-Si- bonds. The increase in the intensity of the Q3 resonance relative to that for Q4 also indicates -Si-O-Si-

bond breakage. The increased sharpness of the resonances from the wet material is indicative of increased molecular motion for the silanol species. Thus, we can conclude that the mobility of the coupling agents is increased at both ends of the molecule. This effect is the same even when the sample is a composite and the water has to transport through the polymer matrix. In addition, the bonds appear to reform in more or less the same way as in the original samples when they are dried. It is plausible that this is an important contributing factor in the enhanced stability of composites treated with coupling agents.



## 5. SUMMARY

The use of NMR to study the effects of water on a composite interface has been demonstrated. Since the optical clarity of the sample is not an important factor and the technique can be applied to an actual composite system which is opaque. Through the use of the specific labelling of a coupling agent with deuterium and  $^2\text{H}$  NMR, the interface can be selectively probed in the presence of a carbon-based polymer matrix. Surface selectivity can also be achieved through the use of  $^{29}\text{Si}$  NMR with cross-polarization.

For the coupling agent chemisorbed to silica, the spectra are consistent with rotational Brownian diffusion, plus two-site jump motions. The mechanism of motion dominating the NMR spectrum does not appear to change with the addition of water, but the rate is increased by about a factor of four over the dry system. When BMI is polymerized over the treated surface, the mechanism of motion appears to change to two-site jumps only, with the populations of the two-sites unequal. Water has a significant affect on the interface in this model composite and increases the jump rate by a factor of three over the dry composite. In both cases, the interfaces appear to return to their original state upon drying.

The increased mobility of the interface with the addition of water is not limited to the amine end of the molecule, but the silicon end is also affected. The presence of water speeds up the motion of the silicon atoms of the coupling agents and probably breaks one or more of the Si-O-Si bonds. These also return to their original state upon drying. This breaking and reforming of the Si-O-Si bonds may be fundamental to the mechanism of enhanced performance of composites treated with silane coupling agents. The enhanced mobility of the interface in the presence of water may also be responsible for the degradation of mechanical properties in wet composites as well.

**Acknowledgement** The authors gratefully acknowledge the financial assistant of the Office of Naval Research. We are also grateful to Drs. Wittebort, Schnieder and Freed for supplying line shape simulation programs.

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### Figure Captions

Fig. 1. Experimental and simulated  $^2\text{H}$  solid-echo NMR spectra of DABS on silica: (A) chemisorbed from 2% solution; (B) sample from A treated in boiling  $\text{H}_2\text{O}$ , wet; (C) sample from B, redried. The spectra were simulated based on Brownian rotational diffusion ( $R_{\parallel} = 7.0 \times 10^4 \text{ s}^{-1}$ ,  $R_{\perp} = 1.0 \times 10^4 \text{ s}^{-1}$ ) plus two-site jumps with rates with rates of: (A)  $1.0 \times 10^6 \text{ s}^{-1}$ ; (B)  $4.0 \times 10^6 \text{ s}^{-1}$ ; and (C)  $1.0 \times 10^6 \text{ s}^{-1}$ .

Fig. 2. Experimental and simulated  $^2\text{H}$  solid-echo NMR spectra of DABS on silica with BMI (1.5/1.0 mol ratio) polymerized over it: (A) dry composite; (B) sample from A treated in boiling  $\text{H}_2\text{O}$ , wet; (C) sample from B, redried. The spectra were simulated based on two-site jumps with unequal site populations and rates of: (A)  $1.7 \times 10^5 \text{ s}^{-1}$ ; (B)  $5.0 \times 10^5 \text{ s}^{-1}$ ; and (C)  $1.7 \times 10^5 \text{ s}^{-1}$ .

Fig. 3.  $^2\text{H}$  solid echo NMR spectra of coupling agents chemisorbed on silica. (A) ABS, from 2% solution washed with  $\text{D}_2\text{O}$ , then dried; (B) DABS, from 2% solution (same as Fig. 1A, for comparison).

Fig. 4.  $^{29}\text{Si}$  CP/MAS NMR spectra of DABS adsorbed on silica: (A) dry-air interface; (B) wet-air interface; (C) dry-composite; and (D) wet-composite.

